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(71) Demandeur/Applicant:  
BASF AKTIENGESELLSCHAFT, DE

(72) Inventeurs/Inventors:  
WENDEROTH, BERND, DE;  
DAMBACH, STEFAN, DE;  
MESZAROS, LADISLAUS, DE;  
FIDORRA, UWE, DE

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : REFRIGERANTS DESTINES A DES SYSTEMES DE REFROIDISSEMENT DANS DES ENTRAÎNEMENTS A  
PILES A COMBUSTIBLE ET CONTENANT DES DERIVES D'AZOLE

(54) Title: COOLING AGENTS FOR COOLING SYSTEMS IN FUEL CELL DRIVES CONTAINING AZOLE DERIVATIVES

(57) Abrégé/Abstract:

The invention relates to antifreeze concentrates for cooling systems in fuel cell drives, which are used to produce ready-to-use aqueous cooling agent compositions having a maximum conductivity of 50 µS/cm, based on alkylene glycols or the derivatives thereof, containing one or several five-membered heterocyclic compounds (azole derivatives) with 2 or 3 heteroatoms from the nitrogen and sulphur group which contain no or at the most one sulphur atom and which can include an aromatic or saturated six-membered fusion agent.



## 5 Abstract

An antifreeze concentrate for cooling systems in fuel-cell drives which gives ready-to-use aqueous coolant compositions having a conductivity of at most 50  $\mu\text{S}/\text{cm}$ , based on alkylene glycols or  
10 derivatives thereof and containing one or more five-membered heterocyclic compounds (azole derivatives) having 2 or 3 hetero atoms from the group consisting of nitrogen and sulfur, which contain no or at most one sulfur atom and which may carry a fused aromatic or saturated six-membered ring.

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Coolant comprising azole derivatives for cooling systems in fuel-cell drives

- 5 The present invention relates to coolants for cooling systems in fuel-cell drives, in particular for motor vehicles, based on alkylene glycols or derivatives thereof, which comprise specific azole derivatives as corrosion inhibitors.
- 10 Fuel cells for mobile use in motor vehicles have to be capable of operation even at low outside temperatures of down to about  $-40^{\circ}\text{C}$ . A freezing-protected coolant circuit is therefore vital.

The use of the conventional radiator protection compositions  
15 employed in internal-combustion engines would be impossible in fuel cells without complete electrical insulation of the cooling channels, since these compositions, owing to the salts and ionizable compounds present therein as corrosion inhibitors, have high electrical conductivity, which would adversely affect the  
20 function of the fuel cell.

DE-A 198 02 490 (1) describes fuel cells having a freezing-protected cooling circuit in which the coolant used is a paraffinic isomer mixture having a pour point of below  $-40^{\circ}\text{C}$ .  
25 However, the combustibility of a coolant of this type is disadvantageous.

EP-A 1 009 050 (2) discloses a fuel-cell system for automobiles in which the cooling medium used is air. However, it is  
30 disadvantageous here that air, as is known, is a poorer thermal conductor than a liquid cooling medium.

WO 00/17951 (3) describes a cooling system for fuel cells in which the coolant employed is a pure monoethylene glycol/water  
35 mixture in the ratio 1:1 without additives. Since, owing to the lack of corrosion inhibitors, absolutely no corrosion protection would be present against the metals present in the cooling system, the cooling circuit contains an ion exchanger unit in order to maintain the purity of the coolant and to ensure a low  
40 specific conductivity for an extended time, preventing short-circuits and corrosion. Suitable ion exchangers mentioned are anionic resins, for example of the strongly alkaline hydroxyl type, and cationic resins, for example based on sulfonic acid groups, and other filtration units, for example activated carbon  
45 filters.

## 2

The construction and mode of functioning of a fuel cell for automobiles, in particular a fuel cell having an electron-conducting electrolyte membrane ("PEM fuel cell", "polymer electrolyte membrane fuel cell") is described by way of example in (3), the preferred metal component in the cooling circuit (radiator) being aluminum.

DE-A 100 63 951 (4) describes coolants for cooling systems in fuel-cell drives which comprise orthosilicates as corrosion inhibitors.

The use of azole derivatives, such as benzimidazole, benzotriazole or tolutriazole, as corrosion inhibitors in radiation protection compositions for conventional internal-combustion engines operated with gasoline or diesel fuel has been known for some time, for example from: G. Reinhard et al., "Aktiver Korrosionsschutz in wässrigen Medien", pp. 87-98, expert-Verlag 1995 (ISBN 3-8169-1265-6).

The use of azole derivatives of this type in coolants for cooling systems in fuel-cell drives has not been disclosed hitherto.

The main problem in cooling systems in fuel-cell drives is the maintenance of a low electrical conductivity of the coolant in order to ensure safe and fault-free functioning of the fuel cell and to prevent short circuits and corrosion in the long term.

Surprisingly, it has now been found that the time duration for low electrical conductivity in a cooling system based on alkylene glycol/water, also and in particular if it contains an integrated ion exchanger in accordance with (3), can be significantly extended by the addition of small amounts of azole derivatives. This offers the practical advantage that the time intervals between two coolant changes in fuel-cell drives can be extended further, which is of particular interest in the automobile sector.

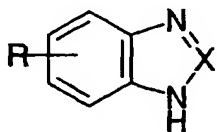
Accordingly, we have found antifreeze concentrates for cooling systems in fuel-cell drives which give ready-to-use aqueous coolant compositions having a conductivity of at most 50  $\mu\text{S}/\text{cm}$ , based on alkylene glycols or derivatives thereof, which comprise one or more five-membered heterocyclic compounds (azole derivatives) having 2 or 3 heteroatoms from the group consisting of nitrogen and sulfur, which contain no or at most one sulfur atom and which may carry a fused aromatic or saturated six-membered ring. Preference is given here to antifreeze concentrates which comprise a total of from 0.05 to 5% by weight,

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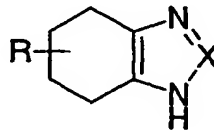
in particular from 0.075 to 2.5% by weight, especially from 0.1 to 1% by weight, of said azole derivatives.

These five-membered heterocyclic compounds (azole derivatives) usually contain, as heteroatoms, two N atoms and no S atom, 3 N atoms and no S atom or one N atom and one S atom.

Preferred groups of said azole derivatives are fused imidazoles and fused 1,2,3-triazoles of the general formula (I) or (II)



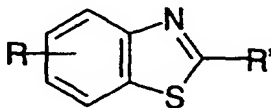
(I)



(II)

where the variable R is hydrogen or a C<sub>1</sub>- to C<sub>10</sub>-alkyl radical, in particular methyl or ethyl, and the variable X is a nitrogen atom or the C-H group. Typical examples of azole derivatives of the general formula (I) are benzimidazole (X = C-H, R = H), benzotriazole (X = N, R = H) and tolutriazole (tolyltriazole) (X = N, R = CH<sub>3</sub>). A typical example of an azole derivative of the general formula (II) is hydrogenated 1,2,3-tolotriazole (tolyltriazole) (X = N, R = CH<sub>3</sub>).

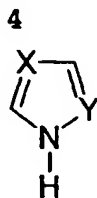
A further preferred group of said azole derivatives comprises benzothiazoles of the general formula (III)



(III)

where the variable R is as defined above, and the variable R' is hydrogen, a C<sub>1</sub>- to C<sub>10</sub>-alkyl radical, in particular methyl or ethyl, or in particular the mercapto group (-SH). A typical example of an azole derivative of the general formula (III) is 2-mercaptobenzothiazole.

Preference is furthermore given to non-fused azole derivatives of the general formula (IV)



(IV)

where the variables X and Y together are two nitrogen atoms or one nitrogen atom and one C-H group, for example  
 10 1H-1,2,4-triazole (X = Y = N) or imidazole (X = N, Y = C-H).

Very particularly preferred azole derivatives for the present invention are benzimidazole, benzotriazole, tolutriazole, hydrogenated tolutriazole or mixtures thereof.

15 Said azole derivatives are commercially available or can be prepared by common methods. Hydrogenated benzotriazoles and hydrogenated tolutriazole are likewise accessible in accordance with DE-A 1 948 794 (5) and are also commercially available.

20 Besides said azole derivatives, the antifreeze concentrates according to the invention preferably additionally comprise orthosilicates, as described in (4). Typical examples of orthosilicates of this type are tetraalkoxysilanes, such as  
 25 tetraethoxysilane. Preference is given here to antifreeze concentrates, in particular those having a total content of from 0.05 to 5% by weight of said azole derivatives, which give ready-to-use aqueous coolant compositions having a silicon content of from 2 to 2000 ppm by weight of silicon, in particular  
 30 from 25 to 500 ppm by weight of silicon.

Dilution of the antifreeze concentrates according to the invention with ion-free water gives ready-to-use aqueous coolant compositions having a conductivity of at most 50  $\mu\text{S}/\text{cm}$  and which  
 35 essentially consist of

- (a) from 10 to 90% by weight of alkylene glycols or derivatives thereof,
- 40 (b) from 90 to 10% by weight of water,
- (c) from 0.005 to 5% by weight, in particular from 0.0075 to 2.5% by weight, especially from 0.01 to 1% by weight, of said azole derivatives, and
- 45 (d) if desired orthosilicates.

The sum of all components here is 100% by weight.

The present invention thus also relates to ready-to-use aqueous coolant compositions for cooling systems in fuel-cell drives  
5 which essentially consist of

(a) from 10 to 90% by weight of alkylene glycols or derivatives thereof,

10 (b) from 90 to 10% by weight of water,

(c) from 0.005 to 5% by weight, in particular from 0.0075 to 2.5% by weight, especially from 0.01 to 1% by weight, of said azole derivatives, and

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(d) if desired orthosilicates.

and which are obtainable by dilution of said antifreeze concentrates with ion-free water. The sum of all components here  
20 is 100% by weight.

The ready-to-use aqueous coolant compositions according to the invention have an initial electrical conductivity of at most 50  $\mu\text{S}/\text{cm}$ , in particular 25  $\mu\text{S}/\text{cm}$ , preferably 10  $\mu\text{S}/\text{cm}$ , especially  
25 5  $\mu\text{S}/\text{cm}$ . The conductivity is kept at this low level in long-term operation of the fuel-cell drive over a number of weeks or months, in particular if a cooling system with integrated ion exchanger is used in the fuel-cell drive.

30 The pH of the ready-to-use aqueous coolant compositions according to the invention drops significantly more slowly over the operating time than in the case of cooling fluids to which said azole derivatives have not been added. The pH is usually in the range from 4.5 to 7 in the case of fresh coolant compositions  
35 according to the invention and usually drops to 3.5 in long-term operation. The ion-free water used for the dilution may be pure distilled or bidistilled water or water that has been deionized by, for example, ion exchange.

40 The preferred mixing ratio by weight between the alkylene glycol or derivatives thereof and water in the ready-to-use aqueous coolant compositions is from 20:80 to 80:20, in particular from 25:75 to 75:25, preferably from 65:35 to 35:65, especially from 60:40 to 40:60. The alkylene glycol component or derivatives  
45 thereof which can be used here is, in particular, monoethylene glycol, but also monopropylene glycol, polyglycols, glycol ethers or glycerol, in each case alone or in the form of mixtures

thereof. Particular preference is given to monoethylene glycol alone or mixtures of monoethylene glycol as the principal component, i.e. with a content in the mixture of greater than 50% by weight, in particular greater than 80% by weight, especially greater than 95% by weight, with other alkylene glycols or derivatives of alkylene glycols.

The antifreeze concentrates according to the invention which give the ready-to-use aqueous coolant compositions described can themselves be prepared by dissolving said azole derivatives in alkylene glycols or derivatives thereof which are water-free or have a low water content (for example up to 10% by weight, in particular up to 5% by weight).

The present invention also relates to the use of five-membered heterocyclic compounds (azole derivatives) having 2 or 3 hetero atoms from the group consisting of nitrogen and sulfur, which contain no or at most one sulfur atom and which may carry a fused aromatic or saturated six-membered ring for the preparation of antifreeze concentrates for cooling systems in fuel-cell drives, in particular for motor vehicles, based on alkylene glycols and derivatives thereof.

The present invention furthermore relates to the use of these antifreeze concentrates for the preparation of ready-to-use aqueous coolant compositions having a conductivity of at most 50  $\mu\text{S}/\text{cm}$  for cooling systems in fuel-cell drives, in particular for motor vehicles.

The coolant compositions according to the invention may also be employed in a fuel-cell unit as described in DE-A 101 04 771 (6), in which the cooling medium is additionally electrochemically deionized in order to prevent corrosion.

### Examples

The invention is explained in the following examples, but without being restricted thereto.

In the test described below, the coolant compositions according to the invention were tested for their suitability for fuel-cell drives in comparison with a coolant composition as described in (3):



## Description of the experiment:

Five aluminum test metals (vacuum-soldered Al, name: EN-AW 3005, solder-plated on one side with 10% by weight of EN-AW 4045; dimensions: 58 x 26 x 0.35 mm with a hole having a diameter of 7 mm) were weighed, connected in a non-conductive manner by means of a plastic screw with washer and Teflon disks and placed on two Teflon stands in a 1 l beaker with ground-glass joint and glass lid. 1000 ml of test liquid were subsequently introduced. In the experiments shown in Table 1 below, a small fabric sack containing 2.5 g of an ion exchanger (AMBERJET® UP 6040 RESIN mixed bed resin ion exchanger from Rohm + Haas) was suspended in the liquid, and the examples in Table 2 shown below were carried out without the presence of an ion exchanger. The beaker was sealed in an air-tight manner with the glass lid and heated to 88°C, and the liquid was stirred vigorously using a magnetic stirrer. The electrical conductivity was measured at the beginning of the test and at intervals of several weeks on a liquid sample taken in advance (LF 530 conductivity meter from WTW/Weilheim). After completion of the test, the aluminum samples were assessed visually and, after pickling with aqueous chromic acid/phosphoric acid, evaluated gravimetrically in accordance with ASTM D 1384-94.

The results are shown in Tables 1 and 2.

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Table 1: Experiments in the presence of ion exchanger

| Coolant composition:             | Comparative Example   | Example 1:  | Example 2:   | Example 3:  | Example 4:  | Example 5:   |
|----------------------------------|---|---|--|---|---|--|
|                                  | (acc. to WO 00/17951):<br>60 vol.-% MEG<br>40 vol.-% MEG<br>water | 60 vol.-% MEG<br>40 vol.-% water<br>0.1% by wt. benzimidazole | 60 vol.-% MEG<br>40 vol.-% water<br>0.1% by wt. benzo-triazole | 60 vol.-% MEG<br>40 vol.-% water<br>0.1% by wt. tolu-triazole | 60 vol.-% MEG<br>40 vol.-% water<br>0.1% by wt. hydro-genated tolu-triazole | 60 vol.-% MEG<br>40 vol.-% water<br>0.05% by wt. benzo-triazole<br>371 ppm by wt. tetra-ethoxysilane |
| Electrical conductivity [mS/cm@] |   |   |  |   |   |  |
| Beginning of test:               | 2.0   | 4.9   | 3.3  | 3.1   | 1.1   | 1.9  |
| after 7 days:                    | 2.3   | 4.2   | 1.5  | 1.5   | 0.8   | 1.5  |
| after 35 days:                   | ---   | 7.6   | 4.1  | 10.2  | ---   | 2.5  |
| after 42 days:                   | 36.2  | ---   | 3.9  | ---   | 3.5   | 3.3  |
| after 56 days:                   | ---   | ---   | 7.8  | ---   | ---   | 5.5  |
| pH                               |   |   |  |   |   |  |
| Beginning of test:               | 6.9   | 7.5   | 5.0  | 5.5   | 6.6   | 5.5  |
| End of test:                     | 2.9   | 6.5   | 3.8  | 3.9   | 4.0   | 3.7  |

| Appearance of<br>aluminum samples<br>after the test:      | slightly<br>tarnished | tarnished          | tarnished           | tarnished           | tarnished           | tarnished           |
|---|-----------------------|--------------------|---------------------|---------------------|---------------------|---------------------|
| Weight change<br>[mg/cm <sup>2</sup> ]<br>after pickling: |                       |                    |                     |                     |                     |                     |
| 1   | - 0.05                | -0.07              | - 0.06              | -0.01               | - 0.04              | -0.03               |
| 2   | - 0.04                | -0.06              | - 0.06              | -0.01               | - 0.05              | -0.04               |
| 3   | - 0.04                | -0.06              | - 0.06              | -0.01               | - 0.05              | -0.02               |
| 4   | - 0.04                | -0.06              | - 0.06              | -0.01               | - 0.05              | -0.03               |
| 5   | - 0.03                | -0.07              | - 0.06              | -0.01               | - 0.05              | -0.03               |
| Mean of the samples                                       | - 0.04                | -0.06              | - 0.06              | -0.01               | - 0.05              | -0.03               |
| Solution at end of<br>test                                | yellowish,<br>clear   | brownish,<br>clear | colorless,<br>clear | colorless,<br>clear | colorless,<br>clear | colorless,<br>clear |

In the mixture of monoethylene glycol (= MEG) and water, the volume ratio of 60:40 corresponds to a weight ratio of 62.5:37.5.

In Example 5 according to the invention, the orthosilicate was metered in so that a silicon content of 50 ppm by weight was present in the cooling liquid.

The results in Table 1 show that a very low electrical conductivity of less than 4  $\mu\text{S}/\text{cm}$  was present even after an uninterrupted experiment duration of 42 days in Examples 2 and 4 in accordance with the invention, while, with an increase to virtually 40  $\mu\text{S}/\text{cm}$ , a significant impairment had occurred in the coolant with no additives in accordance with WO 00/17951 (3). Even after an uninterrupted experiment duration of 56 days, the electrical conductivity was in some cases still significantly below 8  $\mu\text{S}/\text{cm}$  in Examples 2 and 5 in accordance with the invention.

In no case did significant corrosion on the aluminum samples occur.

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Table 2: Experiments without ion exchanger

|    |  |   |  |  |
|----|--|---|--|--|
| 20 | Coolant composition:                                   | Example 1:<br>60 vol.-% MEG<br>40 vol.-%<br>water<br>0.1% by wt.<br>benzotriazole | Example 2:<br>60 vol.-% MEG<br>40 vol.-% water<br>0.1% by wt.<br>benzotriazole<br>742 ppm by wt.<br>tetraethoxy-<br>silane | Example 3:<br>60 vol.-% MEG<br>40 vol.-%<br>water<br>0.1% by wt.<br>hydrogenated<br>tolutriazole |
| 25 | Electrical conductivity<br>[ $\mu\text{S}/\text{cm}$ ] |   |  |  |
| 30 | Beginning of<br>test:                                  | 3.2   | 3.2  | 2.1  |
|    | after 7 days:  | 5.0   | 5.6  |  |
|    | after 14 days:   | 5.8   | 5.2  | 5.8  |
|    | after 28 days:   | 8.2   | 6.9  |  |
|    | after 35 days:   | 11.2  | 6.9  | 8.6  |
| 35 | after 42 days:   | 13.1  | 7.9  | 9.3  |
|    | after 49 days:   | 16.1  | 7.6  | 9.7  |
|    | after 56 days:   | ---   | 7.8  |  |
|    | after 63 days:   | ---   | 7.1  |  |
|    | after 77 days:   | ---   | 6.6  | 17.5   |
| 40 | pH   |   |  |  |
|    | Beginning of<br>test:                                  | 5.0   | 5.0  | 5.2  |
|    | End of test:   | 3.6   | 4.9  | 3.4  |

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|    |   |                     |                     |                     |
|----|---|---------------------|---------------------|---------------------|
|    | Appearance of<br>aluminum samples<br>after the test:      | almost<br>unchanged | almost unchanged    | tarnished           |
| 5  | Weight change<br>[mg/cm <sup>2</sup> ]<br>after pickling: |                     |                     |                     |
|    | 1   | -0.01               | 0.00                | - 0.02              |
|    | 2   | 0.00                | 0.00                | - 0.02              |
|    | 3   | 0.00                | 0.00                | - 0.04              |
| 10 | 4   | 0.00                | 0.00                | - 0.04              |
|    | 5   |                     |                     |                     |
|    | Mean of the<br>samples                                    | 0.00                | 0.00                | - 0.03              |
| 15 | Solution at end<br>of test                                | colorless,<br>clear | colorless,<br>clear | colorless,<br>clear |

In the mixture of monoethylene glycol (= MEG) and water, the volume ratio of 60:40 corresponds to a weight ratio of 62.5:37.5.

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In Example 2 according to the invention, the orthosilicate was metered in such that a silicon content of 100 ppm by weight was present in the cooling liquid.

25 The results from Table 2 show that a very low electrical conductivity of significantly less than 10  $\mu\text{S}/\text{cm}$  was present even after an uninterrupted experiment duration of 77 days in Example 2 in accordance with the invention; the electrical conductivity after 77 days was again significantly below 20  $\mu\text{S}/\text{cm}$  in Example 3

30 in accordance with the invention.

In these experiments too, no or no significant corrosion occurred on the aluminum samples.

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## Amended claims:

1. An antifreeze concentrate for cooling systems in fuel-cell  
5 drives which gives a ready-to-use aqueous coolant composition  
having a conductivity of at most 50  $\mu\text{S}/\text{cm}$ , based on alkylene  
glycols or derivatives thereof and containing one or more  
five-membered heterocyclic compounds (azole derivatives)  
having 2 or 3 heteroatoms from the group consisting of  
10 nitrogen and sulfur, which contain no or at most one sulfur  
atom and which may carry a fused aromatic or saturated  
six-membered ring, and additionally orthosilicates which give  
a ready-to-use aqueous coolant composition having a silicon  
content of from 2 to 2000 ppm by weight.
- 15 2. An antifreeze concentrate for cooling systems in fuel-cell  
drives as claimed in claim 1, comprising a total of from 0.05  
to 5% by weight of the azole derivatives.
- 20 3. An antifreeze concentrate for cooling systems in fuel-cell  
drives as claimed in claim 1 or 2, comprising, as azole  
derivatives, benzimidazole, benzotriazole, tolutriazole  
and/or hydrogenated tolutriazole.
- 25 4. An antifreeze concentrate for cooling systems in fuel-cell  
drives as claimed in any one of claims 1 to 3, in which the  
alkylene glycol employed is monoethylene glycol.
5. An antifreeze concentrate for cooling systems in fuel-cell  
30 drives as claimed in any one of claims 1 to 4, which gives,  
on dilution with ion-free water, a ready-to-use aqueous  
coolant composition having a conductivity of at most 50  $\mu\text{S}/\text{cm}$   
and which essentially consists of
  - 35 (a) from 10 to 90% by weight of alkylene glycols or  
derivatives thereof,
  - (b) from 90 to 10% by weight of water,
  - 40 (c) from 0.005 to 5% by weight of the azole derivatives, and
  - (d) orthosilicates in an amount which gives a ready-to-use  
aqueous coolant composition having a silicon content of  
from 2 to 2000 ppm by weight.

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6. A ready-to-use aqueous coolant composition for cooling systems in fuel-cell drives which essentially consists of
- (a) from 10 to 90% by weight of alkylene glycols or derivatives thereof,
- (b) from 90 to 10% by weight of water,
- (c) from 0.005 to 5% by weight of the azole derivatives, and
- (d) orthosilicates in an amount which gives a ready-to-use aqueous coolant composition having a silicon content of from 2 to 2000 ppm by weight,
- obtainable by dilution of an antifreeze concentrate as claimed in any one of claims 1 to 4 with ion-free water.
7. The use of a five-membered heterocyclic compound (azole derivative) having 2 or 3 heteroatoms from the group consisting of nitrogen and sulfur, which contains no or at most one sulfur atom and which may carry a fused aromatic or saturated six-membered ring, together with orthosilicates for the preparation of an antifreeze concentrate for cooling systems in fuel-cell drives based on alkylene glycols or derivatives thereof.
8. The use of an antifreeze concentrate as claimed in claim 7 for the preparation of a ready-to-use aqueous coolant composition having a conductivity of at most 50  $\mu\text{S}/\text{cm}$  for cooling systems in fuel-cell drives.